

Improved electro-optical properties of dye-doped polymer dispersed liquid crystal display

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The next generation polymer dispersed liquid crystals (PDLCs) based electro optical devices could be polarizer-free flexible and reflective just by doping the dichroic dye material in such devices. The electro-optical performances of both scattering (Off state) and electrically absorbing On state of dye-doped PDLC depend on the curing properties and compositions of dye mixture that control the contrast ratios and domain sizes of polymer networks. Due to having polymer networks that surrounds the LC droplets such electro-optical devices are flexible. In the present work, a dichroic black dye S428 is utilized in PDLC system to make it colored with enhanced contrast ratio properties. Three types of PDLC devices with cell thickness of 20 μ m are fabricated by different LC and Polymer contents. The doping contents of dye have been varied from 0.5 to 1.5 wt% into the PDLC films. The dye S428 (1.5 wt%) has exhibited smaller domain size PDLCs consisting the ratios of LC/Polymer 77:23 wt% and has indicated the higher contrast ratio and lower operational voltage. This dye can be a distinctive addition in dye doped PDLCs for optical applications.

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1. Introduction

Polymer-dispersed liquid crystals (PDLCs) represent an important new class of materials with electro-optical applications such as flexible displays, large-area projection displays, electrically switchable windows etc. [1-5]. These PDLC devices have edge over than conventional liquid crystal display (LCD) as they do not require polarizers [1, 4]. In the most common format PDLCs are consists of micron sized domains of liquid crystals that are randomly dispersed in a polymer matrix. These domains are usually in the form of droplets. PDLCs can be prepared in several different ways; the well-known methods are encapsulation and phase separation. Each method produces PDLCs with different properties such as droplets morphologies and electro optical characteristics [6-12].

Another renowned PDLC device that have been greatly studied for colored optical shutter applications as have higher reflectivity, wide viewing angle and low power consumption properties. These devices are commonly known as dye doped PDLC (DD-PDLC) in which the dichroic dye is doped into PDLC film in small concentration [13-17]. The projection image of DD-PDLC is shown in Fig.1. However, these DD-PDLCs have some limitations, such as low contrast ratio (CR) and higher threshold (V_{th}) and saturation voltages due to higher solubility and higher absorption of UV light by dichroic dye molecules [18-21].

In this study, an effort has been made to examine less studied black dichroic dye S428 (supplied from Mitsui Chemical Co.) in polymer dispersed liquid crystal (PDLC)

systems of LC (TL203) and monomer (PN393) on varying the compositions of PDLC mixture as well as the dye contents. The aim was to find optimum properties such as high contrast ratio, low V_{th} in various PN393, LC and dichroic black dye compositions.

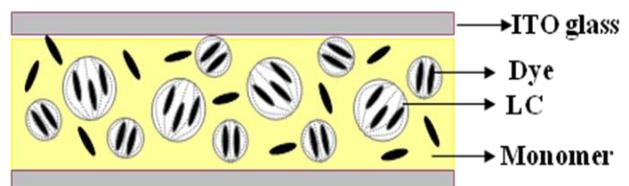


Fig. 1. Projection of dye doped PDLC display

2. Experimental work

The Dye doped PDLC (DD-PDLC) devices are fabricated by sandwiching a mixture of pre-polymer, liquid crystal and dye in between the transparent indium tin oxide (ITO) coated glass plates with a 20 μ m cell gap thickness. The mixtures of LC, pre-polymer and dye is prepared by using TL203 (Merck), PN393 (Merck) and S-428 (Mitsui) black dye at different compositions 80:20 to 75:25 by weight. The various dye compositions are prepared by mixing the dye from 0.1-1.5 wt% in LC. Further, this mixture of TL203 and PN393 is filled in this ITO device by capillary rise method. This is further polymerized by illuminating it with a UV lamp ($\lambda \sim 365$

nm) with intensity of 1 mW/cm^2 for 20 minutes at 26°C temperature.

2.1. Experimental measurements

The electro-optical experiments (transmittance and contrast ratios) are performed at room temperature by measuring the transmission of un-polarized HeNe laser light at wavelength range $\lambda = 400\text{-}700 \text{ nm}$ by using Minolta UV-Vis spectrophotometer (model UV-3500d, Japan). The DD-PDLC films are oriented normal to the laser beam. The distance between the sample cell and the detector is fixed approximately 38 cm. The collection angle of the transmitted intensity is set about 0° , so that principally forward scattering is detected. The transmission measurements are corrected by using appropriate calibration standards. For measuring sample transmittance (T) against applied voltage curves, external electric field is applied across the DD-PDLCs. The transmittance against the applied voltage is measured by Minolta UV-Vis spectrophotometer as connected with the PC. The surface morphologies of the DD-PDLC films are viewed by polarized optical microscope (Olympus Model BX-60) at 20x magnification fitted with a digital camera connected to a computer.

3. Results and discussions

3.1. Morphologies

For the investigation of optimal properties of S-428 dye doped PDLC display, initially different compositions of TL203, PN393 were selected with fixed 1 wt% of dye. Following this, three DD-PDLCs were made having weight ratios of LC with monomer as 75:25, 77:23 and

80:20 at 26°C . The morphologies for the following DD-PDLC have been mentioned in Fig. 2. Fig. 2(a-c) shows observed LC droplet morphologies from optical microscope at 20x magnification of polarized optical microscope (POM) at voltage off-state for dye-doped PDLC (DD-PDLC) devices at varied LCs compositions, such as 80, 77 and 75 wt% respectively; whereas the concentrations of dichroic dye was fixed at 1 wt%. Fig. 2(a-c) shows the increase in droplet size of DD-PDLC with the addition of LC contents. The increase in droplet size can be more clearly seen for 80 and 77 wt% LC contents. The Fig. 2(c) displays smaller sized random distribution of LC droplets at lower LC concentration (75 wt %) than those at the higher concentration of LC (80-77 wt %) for 1 wt% dye contents. Besides this, as the LC contents were increased the larger LC droplets were observed (80 wt %) that showed little coalescence of LC droplets. This was because of rate of polymerization. Probably at the onset of polymerization, the DD-PDLC mixture moved closer to the phase boundary. In addition to the absorption of UV light by dye molecules it resulted in a less developed polymer matrix during phase separation and this resulted into longer time for the LCs to form large domains and thus coalescence was observed. Earlier it was established that for enhanced light scattering properties the homogeneity and size of LC droplet comparable to the wavelength of scattered light was considered essential [22]. Further for the less LC contents (77 wt%, 75 wt%) the DD-PDLC showed smaller LC droplets with decreased in LC contents (Fig. 2 (b, c)). The smaller droplets formation in low LC contents was possibly due to caged LC molecules in complex structure of polymer matrix [6, 23-24]. This enabled less free volume for the dispersed LC molecules [25]. Previously, the decrease in droplet size with decrease in LC weight fraction was also observed and this was explained by changes in the extent of polymerization at the onset of phase separation [6, 23-24].

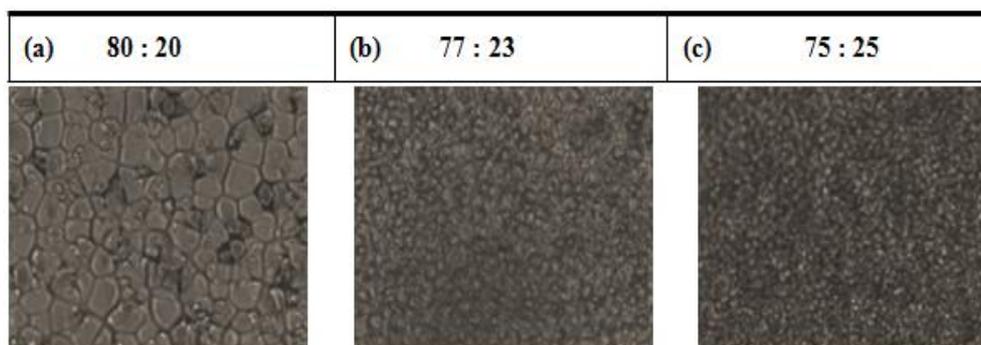


Fig. 2. The surface morphologies of dye doped PDLC having 1 wt% S428 with LC/monomer compositions as (a) 80:20 wt%, (b) 77:23 wt% and 75:25 wt% respectively

It is known that, both droplets shape and LC configuration play key roles in governing the light-scattering properties of DD-PDLC devices [1]. Fig. 3 shows POM images at 20x magnification of dye PDLC taking LC and PN393 ratio fixed at 77 wt%, while varying the dye concentration from 0.5 wt to 1.5 wt %. The 77 wt% DD-PDLC was only selected for further studies due to its optimal droplet morphology at 1 wt% of dye (as

shown previously). Figure 3 shows the increase in droplet size of DD-PDLC with the addition of dye from 0.5 wt% to 1.5 wt%. The Fig. 3(a) displays DD-PDLC having 0.5 wt% dye of smaller droplet size and more uniform distribution of LC droplets as compared to those at the higher concentration of dye (1wt% and 1.5 wt%) for 77 wt% of LC contents. As described earlier the smaller droplet size lead to higher scattering to DD-PDLC devices

[22]. Moreover, Fig. 3 b-c showed enlarged LC droplets as the dye contents increased. This increase in droplet size with increase of dye contents was believed to be due to absorption of UV light by dichroic dye molecules. Dye molecules in the DD-PDLC devices at the onset of phase

separation absorbed UV light and this absorbance increased with the increase of dye concentration [26]. Thus, less intensity of UV light remained there that produced the slower phase separation process. This in turn produced enlarged LC droplets.

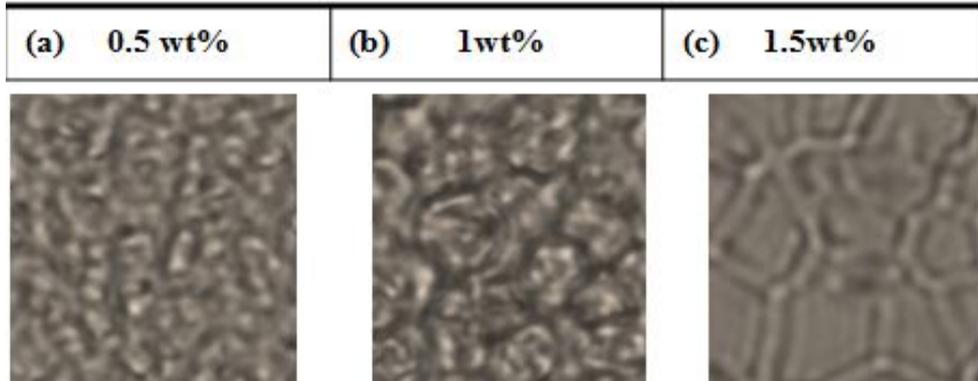


Fig. 3. The surface morphologies of dye doped PDLC having 77:23 wt% of LC/monomer while S428 with compositions as (a) 0.5 wt%, (b) 1 wt% and 1.5 wt% respectively.

3.2. Electro-optical properties

A voltage-transmittance (V-T) characteristic was measured for various DD-PDLC devices at various LC/monomer concentrations at fixed 1 wt% of dye S428. Fig. 4a shows the transmittance curves of dye-doped PDLC for 1 wt% of dye while LC/monomer contents were varied from 80:20 to 75:25 weight ratio. The minimum transmittance, maximum transmittance, the contrast ratio, threshold voltage and driving voltage were generally chosen as T_0 , T_{sat} , CR, V_{th} , V_{on} , respectively. The Table 1 showed all the following values for dye doped PDLCs. Fig. 3a showed that DD-PDLC at lower LC contents (75 wt%) produce higher scattering black state at voltage off (zero voltage). In addition to this, the transmittance at zero voltage was increased with the increase of LC contents (77 wt% and 80 wt%) for DD-PDLC films for dye 1 wt%. Earlier, it was established, that this increase in transmittance was due to increase in droplet size that in turn produce less scattering to the transmitted light. This can be confirmed from the Fig. 2 that the increase in droplet sizes of DD-PDLC at fixed dye contents while raising LC/monomer contents.

Besides this, Fig. 4a showed that maximum transmittance was improved with the increase of LC contents. This behavior was related to the anchoring energies and intermolecular forces. The following forces can be decreased when the droplet size is essentially large. Hence, the higher LC contents DD-PDLC device showed higher transmittance with larger droplet size. The contrast ratio (CR) of a dichroic PDLC film is an important parameter to measure the performance of any electro-optical devices.

Table 1. The electro optical properties of DD-PDLC display using S428 dye

SAMPLES	T_0 (%)	T_{on} (%)	CR (20 V)	V_{th} (V)	V_{on} (V)	
LC/monomer (wt%)						
S428 (1 wt%)	80:20	13	85.20	4.68	4.1	19.3
	77:23	9	77.20	5.44	4.8	20.68
	75:25	4	33.34	2.71	14.4	22.06
Dye contents (wt%)						
LC: monomer (77:23 wt%)	0.5	7	82.20	11.74	8.95	19.99
	1	9	77.20	8.57	8.27	21.37
	1.5	5	60.44	12.07	6.19	20.69

The contrast ratio as a function of LC concentration and applied voltage with fixed dye contents were plotted in Fig. 4b. The contrast ratios (CR) of dichroic dye PDLC as measured at various applied voltages (Fig. 4b) showed an increase in CR with the increase of applied voltage and attained a maximum value. However further increase in voltage the CR remained as constant. Fig. 4b showed that contrast ratio of DD-PDLC was decreased with the addition of LC contents. General analysis of the Fig. 4b showed that as compared to high LC contents, lower LC contents exhibited high contrast ratio. The reason for this behavior was attributed to the droplet morphologies that were formed by varying the LC contents. The device with higher LC contents showed more transmittance at On state of electric field due to less anchoring forces but less scattering at zero voltage due to bigger droplet size; thus exhibited less CR values.

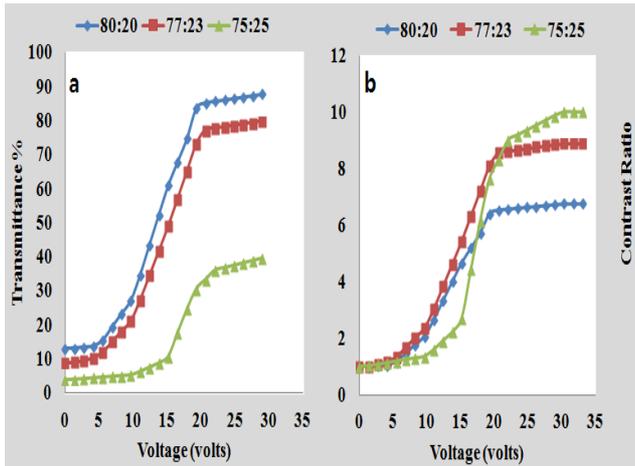


Fig. 4. Electro optical properties of DD-PDLC: (a) Volt transmittance curve, (b) Contrast ratio at various LC/monomer compositions

For bipolar configuration of LC droplets, an expression for V_{th} and V_{on} were explained as [7-8, 25]

$$V_{th} \propto \sqrt{\frac{k}{\Delta\epsilon}} \quad (1)$$

$$V_{on} = \frac{d}{R} \sqrt{\frac{k(\omega^2 - 1)}{\epsilon_0 \Delta\epsilon}} \quad (2)$$

Where d was the film thickness, R was the average droplet radius, K denoted splay elastic constant, ω was the aspect ratio of droplet, ϵ_0 was the vacuum dielectric constant and $\Delta\epsilon$ denoted the dielectric anisotropy of the LCs. The threshold voltage (V_{th}) may depend on anchoring energies and intermolecular interactions as well as, on the elastic constant and dielectric anisotropy [27]. Table 1 showed the V_{th} and V_{on} values for different dye contents. It was found that increase of LC contents while dye has fixed amount (1 wt%) lead to decrease in the V_{th} of DD-PDLC. The decrease in V_{th} also depended on the anchoring forces that may reduce with the increase in droplet size. Thus, V_{th} decreased with increase in LC contents. The equation (2) showed that the driving voltage, V_{on} depended on droplet size, film thickness, elastic constant and dielectric anisotropy. According to V_{on} was inversely proportional to droplet diameter, as long as the droplet size was kept small compared with film thickness [27]. For S428 dye the V_{on} was found to increase with decrease in droplet size. The increase in V_{on} for very small droplet size was due to high surface anchoring energy of very small droplet size. These findings bring to a clue that the dye doped PDLC formed with 77:23 wt% have optimum electro-optical properties and can be selected for further studies with different dye contents.

The Fig. 5(a,b) showed the voltage-transmittance (V-T) characteristic for DD-PDLC at various dye concentrations while LC contents were fixed (77 wt%). Fig. 5a showed the transmittance curves against the voltage for dye-doped PDLC having 0.5 wt%, 1 wt%, and

1.5 wt% of dye. The minimum transmittance, maximum transmittance, contrast ratio, threshold voltage and driving voltage are mentioned in table 1. Fig. 5a showed that dye doped PDLC produced higher scattering (T_{off}) for 1.5 wt% (5% transmittance) and then little increase for 0.5 wt% (7% transmittance) and 9% transmittance for 1 wt%. Moreover, T_{on} was found to be decreased with increase in dye contents. A little increase in V_{th} and V_{on} with increase in dye contents were observed that was established earlier due to higher absorption of UV light with increase in dye concentration [25].

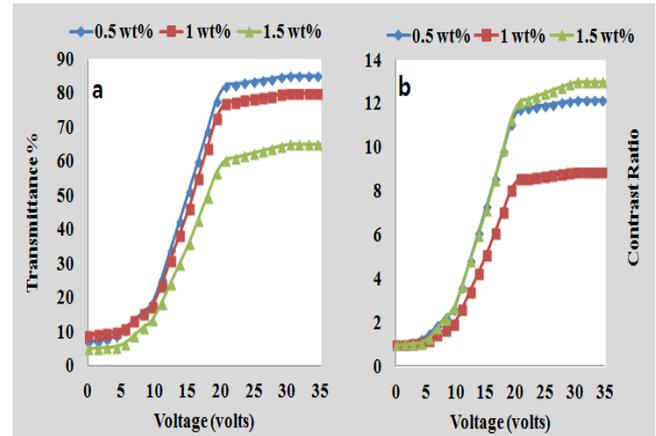


Fig. 5. Electro optical properties of DD-PDLC: (a) Volt transmittance curve, (b) Contrast ratio at various dye concentrations

Furthermore, Fig. 5b showed the contrast ratios of following dye doped PDLCs. This showed higher CR values (13) for higher dye contents at V_{on} state. Moreover, less CR values for 0.5 wt% (12.14) and 1 wt% (8.89) of dye were observed. However, this dye S428 was overall found as a good new candidate in dye doped PDLC with higher CR values and V_{th} less than 10 volts. These results revealed less solubility of dye with monomer and low absorption of UV light that further enhance the electro-optical properties of dye PDLCs.

4. Conclusions

In this work, a less studied black dichroic dye S428 has been used with TL203 LC and PN393 monomer to fabricate a dye-doped PDLC display. It was found that the following dye showed good electro optical properties such as CR and V_{th} while on using low LC contents and higher dye concentration. This can be taken as achievement in dye doped PDLCs, since in earlier studies the electro optical properties declined as the dye contents increased or LC contents decreased. However, a general trend in morphologies of dye doped PDLC was observed as increase in droplet size with the increase in dye contents, while LC contents were kept constant. The following results projected that this dye has the ability to significantly enhance the electro-optical properties of DD-PDLC with suitable selection of LC and dye weight

fractions. This dye-doped PDLC display has opened a new window for trim-able electronic papers, decorative displays, electrically switchable curtains, and electrically switchable sun control films for the automobiles, homes or commercial buildings.

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References

- [1] P. S. Drzaic, Liquid crystal dispersions (Singapore: World Scientific) **1**, 22, (1995).
- [2] J. L. Fergason, US Patent No. 4435047 (1984).
- [3] A. Masutani, T. Roberts, B. Schüller, N. Hollfelder, P. Kilickiran, G. Nelles and A. Yasuda, Appl. Phys. Lett. **89**, 183514 (2006).
- [4] F. Simoni, Non linear optical properties of LC & PDLCs (Singapore: World Scientific), (1997).
- [5] F. Simoni, O. Francescangeli, Int. J. Polym. Mater. **45**, 381 (2000).
- [6] J-W. Han, T. J. Kang, G. Park, J. Korean Phys. Soc. **36**, 156 (2000).
- [7] A. Farzana, M. Jamil, Y. J. Jeon, Lee J. Woo, Jae E. Jung, Jae E. Jang, Gae H. Lee, Jin S. Park, J App Polym. Sci. **121**, 1424 (2011).
- [8] A. Farzana, M. Jamil, Y. J. Jeon, Current science **101**(11), 1467 (2011).
- [9] A. Farzana, M. Jamil, J. W. Lee, Y. J. Jeon, Colloid Polym. Sci. **290**, 599 (2012).
- [10] A. Farzana, M. Jamil, Y. H. Ri, J. W. Lee, Y. J. Jeon, J. Mod. Opt. **61**(12), 1027 (2014).
- [11] A. Farzana, M. Jamil, J. W. Lee, Y. J. Jeon, Materiale Plastice **52**(2), 171 (2015).
- [12] A. Farzana, M. Jamil, J. W. Lee, S. R. Kim, Y. J. Jeon, Electron. Mater. Lett. **12**(5), 685 (2016).
- [13] J. L. Fergason, SID Symposium Digest **16**, 68 (1985).
- [14] J. L. Fergason, A. Calif, US Patent No. 4596445, (1983).
- [15] G. P. Montgomery, N. A. Vaz, Appl. Opt. **26**, 738 (1987).
- [16] S. H. Lee, T. K. Lim, S. T. Shin, K. S. Park, Jpn. J. Appl. Phys. **41**, 208 (2002).
- [17] Y. H. Lin, H. Ren, S. T. Wu, Appl. Phys. Lett. **84**, 4083 (2004).
- [18] J. E. Jung, G. H. Lee, J. E. Jang, K. Y. Hwang, A. Farzana, M. Jamil, J. W. Lee, Y. J. Jeon, Adv. Sci. Letts. J. **18**(5), 225 (2012).
- [19] J. E. Jung, G. H. Lee, J. E. Jang, K. Y. Hwang, A. Farzana, M. Jamil, J. W. Lee, Y. J. Jeon, Liq. Cryst. J. **39**(11), 1314 (2012).
- [20] J. E. Jung, G. H. Lee, J. E. Jang, K. Y. Hwang, A. Farzana, M. Jamil, J. W. Lee, Y. J. Jeon, J. App. Poly. Sci. **124**, 873 (2012).
- [21] A. Farzana, M. Jamil, J. W. Lee, Y. J. Jeon, J. E. Jung, J. E. Jang, Bull. Mater. Sci. **35**(2), 221 (2012).
- [22] G. H. Springer, D. A. Higgins, J. Am. Chem. Soc. **122**, 6801 (2000).
- [23] J. Lovinger, K.R. Amundson, D. D. Davis, Chem. Mater. **6**, 1726 (1994).
- [24] S. A. Carter, J. D. Le Grange, W. White, J. Boo, P. Wiltzius, J. Appl. Phys. **81**, 9 (1997).
- [25] P. Malik, K. K. Raina, A. M. Bubnov, Mol. Cryst. Liq. Cryst. **494**, 242 (2008).
- [26] G. P. Montgomery, J. L. West, W. J. Tamura-Lis, J. Appl. Phys. **69**, 1605 (1991).
- [27] K-J. Yang, S-C. Lee, B-D. Choi, Jpn. J. Appl. Phys. **49**, 05EA05 (2010).

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